



Review

Where do poly(vinyl alcohol) based membranes stand in relation to Nafion[®] for direct methanol fuel cell applications?

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H I G H L I G H T S

- Development of PVA based membrane for DMFC application.
- Alternate membranes in the near future.
- Examined the data of PVA membranes in the past one decade for DMFC application.
- Commercial feasibility being examined.
- Prescribed appropriate directions for the development of PVA based membranes.

A R T I C L E I N F O

Article history:

Received 16 March 2012

Received in revised form

3 May 2012

Accepted 21 May 2012

Available online 13 June 2012

Keywords:

Poly (vinyl alcohol)

Stability

Durability

Polymer electrolyte membrane

Direct methanol fuel cell

A B S T R A C T

Though fuel cells have been considered as a viable energy conversion device, their adaptation for practical applications has been facing certain challenging issues regarding the availability of appropriate materials and components. For low temperature fuel cells, membranes that are cost effective and also competitive to Nafion[®] are the major requirements especially for Direct Methanol Fuel Cells (DMFC). Proton conductivity and methanol crossover are the two main characteristics that are of great concern for the development of suitable, alternate, and viable membranes for DMFC applications, though other factors including environmental acceptability are also important. In this regard, in recent time's poly (vinyl alcohol) based membranes have been developed as a viable alternative. This presentation therefore assesses the technological advances that have been made and the impediments that are faced in this development. This critical assessment exercise, it is presumed, may contribute toward a speedy development of this critical component for a viable fuel cell based energy economy.

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1. Introduction

Energy sources of the future have to be environmentally acceptable and should be energy efficient more than what is obtainable at present. From these points of view, electrochemical energy sources like Fuel Cells (FC), Batteries and Super Capacitors have been knocking the doors far too long. The current trend of fast depletion of fossil fuel sources has been forcing the introduction of alternate energy conversion devices for a variety of mobile and stationary applications. Among the fuel cell options, Proton Exchange Membrane Fuel Cells (PEMFC) has gained momentum

over the others due to reasons like low temperature operation and easy adaptability for a variety of applications.

Fuel cells, essentially, consists of two electrodes and a membrane with all other auxiliary components. While the two electrodes are jointly responsible for the electrochemical combustion of the fuel, the membrane provides the separation between the two electrodes which in a way sustains the necessary concentration gradient in the respective double layers but also accounts for the selective transport of ionic species between the two electrodes so as to complete both the half cell electrochemical reactions.

Among the various options available for use as fuel in an operative fuel cell, methanol is one of the best options other than hydrogen. In this sense, Direct Methanol Fuel Cell (DMFC) has unique opportunity to become a possible and viable option in the near future [1]. Hence developments of components especially membranes for DMFC acquires special importance, in view of the

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fact that fuel transport from anode to cathode side, conventionally termed as methanol crossover has far reaching consequence in deploying DMFC as a viable and economically acceptable energy source.

The selection of membranes for use in fuel cells particularly for DMFC must be made based on a variety of parameters like cost, chemical stability, film forming ability, extent of hydrophilicity, cross linking feasibility, permeability for water. It is also possible to invoke additional parameters like biodegradable, nonhazardous and environmentally benign. A variety of polymer based membranes including Nafion® has been employed and most of them are deficient in relation to methanol crossover in DMFC.

A schematic representation of a membrane and various processes driven by it are given in Fig. 1 [2]. Membranes often respond to a few gradients that they experience between either sides of the membrane. If concentration is the gradient, the process dialysis results; if pressure is the gradient, then reverse osmosis, ultra filtration, micro filtration or nano filtration result. If potential is a gradient then it drives processes such as electro-dialysis or electrophoresis.

It is possible to exploit various parameters in the development of membranes and among them the electrical conductivity of the developed membrane has received considerable attention, however, in the specific application, the species transfer across the membrane can be another factor for consideration in the development of membrane for electrochemical device applications such as fuel cells, batteries and water electrolysis cells. In electrochemical cells the membranes has to act in addition to its established function of molecular sieve, they also play key roles like it separates the two electrodes, it prevents mixing of fuel and oxidant and it also provides a conductive pathway. In the case of electric field gradient, the membranes have to face some usual challenges. Membranes have not withstand pressure gradients (mechanical stability) as well as to exhibit stability under the rigorous chemical environments (chemical stability). The desirable properties of a material to be chosen as a membrane for fuel cell application are:

- High proton conductivity and zero electronic conductivity
- Electrochemical and chemical stability at elevated temperatures in both oxidizing and reducing environments

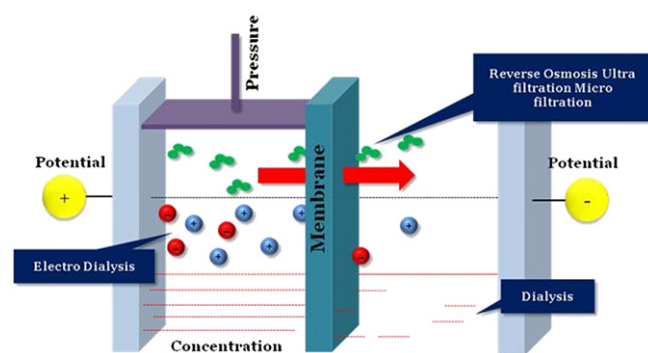


Fig. 1. Schematic representation of a membrane and processes therein [2].

- Adequate mechanical strength, preferably resistance to solvent swelling
- Adequate barrier to oxidant and fuel crossover
- Cost effective and readily available.

Based on these governing characteristics, membranes have been developed ever since 1959 for fuel cell applications. There are a variety of commercial polymers available today for such applications and the essential data on the commercially available membranes are collected in Table 1. Even though, commercial polymeric membranes have been based on perfluorosulphonic acid (typical one being Nafion), a variety of other membranes like modified sulfonated polymers, polymers based on aromatic hydrocarbons, acid base polymers and organic and inorganic composite membranes has been developed and many of them show limitations in the use in fuel cells. These aspects have been addressed in a publication by Viswanathan and Helen questioning is nafion, the only choice? [3].

Polyvinyl alcohol (PVA) based membranes are one such class which has been receiving increasing attention in DMFC application. If the research activities in the development of PVA membranes are to be intensified especially for DMFC application, then there is urgent need to assess the progress that has already been made in this area so that appropriate and achievable research directions are

Table 1
Characteristics of commercial polymer membranes.

Membrane	Membrane type	Dry thickness (μm)	Equivalent weight (gmol ⁻¹ SO ₃ ⁻¹)	Water content (wt %)	Conductivity (S cm ⁻¹)	Manufacturer
Aciplex-S	Perfluoro sulfonic acid	120	1000	43	0.108	Asahi Chemical
BAM 3G		140(wet)	375–920	87	—	Ballard
Dow		125	800	54	0.114	Dow Chemical
Flemion		50	1000	38	0.14	Asahi Glass
Gore Select		5–20	900–1100	32–43	0.028–0.096	Gore
Nafion® 105		125	1000	—	—	Du Pont
Nafion® 112		50	1100	20.7 ± 0.5	0.065	
Nafion® 1135		89	1100	21.1 ± 0.6	0.11	
Nafion® 115		127	1100	21.9 ± 0.6	0.09	
Nafion® 117		183	1100	23.2 ± 0.4	0.08	
Nafion® 1110		254	1100	38	—	
NRE-211	Perfluoro sulfonic acid /	25.4	—	5.0 ± 0.3	0.1	
NRE-212	PTFE copolymer	50.8	—	5.0 ± 0.3	0.1	
Sterion®L180	Perfluoro sulfonic acid	180	—	—	—	David Fuel cell Components
IonClad®R1010	Tetra-fluoroethylene grafted poly(styrene sulfonic acid)	40	—	—	0.07	Pall Gelman Sciences
IonClad®R4010	Tetrafluoroethylene/perfluoropropylene copolymer	20	—	—	0.08	
CRA	Polyethylene-Tetrafluoroethylene grafted sulphonyls	160	—	—	0.045	Solvay
CRS	Tetra-fluoroethylene with poly(styrene sulfonic acid)	160	—	—	0.05	

evolved. Therefore the strategy that has been adopted for this presentation is to examine in detail the methodologies (synthesis, modifying techniques and performance evaluation) evolved and to examine the other possibilities that can be exploited in the future.

1.1. Chemistry of polyvinyl alcohol (PVA)

Polyvinyl alcohol was made by Herman and Haehnel in 1924 by the hydrolysis of polyvinyl acetate in ethanol with potassium hydroxide. The commercial production of PVA is based on the hydrolysis of the acetate by ester interchange with methanol in the presence of anhydrous sodium methylate or aqueous sodium hydroxide [4]. PVA is an odorless, non toxic, translucent, white or cream colored granular powder. It is a water-soluble polymer that readily reacts with different cross linking agents to form gel. It is also biocompatible and biodegradable. It is also widely used in medical, cosmetic, and packaging applications. PVA shows excellent insulation property as a polymer material; its highest conductivity can reach a value of $10^{-10} \text{ S cm}^{-1}$. In these materials, the doped-impurity ions act as primary charge carriers. PVA membranes have also been used in alcohol dehydrating agent especially for the alcohol-water azeotrope. Since it has high selectivity for water to alcohol, it can effectively reduce the methanol crossover through the membrane when used in direct methanol fuel cells (DMFCs). Therefore, it can be expected that PVA based composite membranes if optimized properly can serve as a potential alternative polymer electrolyte membrane for DMFC applications. All other essential characteristics of this polymer membrane are summarized in Fig. 2 especially in terms of properties and modifications that are feasible. The data on essential characteristics for a membrane application like conductivity, ion exchange capacity, water uptake and methanol permeability for various modifications of PVA based polymers are given in Table 2.

1.2. Modification of PVA

Pure PVA does not possess any protonic conductivity. It is necessary for use in fuel cells the membrane should possess ionic conductivity. It is possible to induce protonic conductivity in PVA by sulfonating the polymer with suitable sulfonating agents like concentrated sulfuric acid, sulfosuccinic acid [5], sulfophthalic acid [6], sulfoacetic acid [7] and chlorosulfonic acid. Some of the sulfonating agents with carboxylic function can also induce cross linking (Fig. 3). Special reagents like lithium organic intermediates which can create special sites for sulfonation have also been employed [8,9]. However, this methodology though gives water

soluble polymer; the extent of cross linking is dependent on the post sulfonation step. Instead of this, it is possible to sulfonate the monomer before polymerization and this method has certain advantages like presence of number controllable functional groups, but the polymer generated is usually water soluble and hence may not find extensive use for the production of membranes.

1.2.1. Modification by copolymerization

There are alternate methods for improving the membrane properties like high proton conductivity, (by increasing of the amount of sulfonating agent employed) better mechanical strength (by the extent of cross linking) and low water solubility (by incorporating hydrophobic components). One of the ways is to couple both hydrophilic and hydrophobic components and copolymerizing them or do a chemical grafting induced by irradiation or chemical activation. A brief selected summary of the attempts that have been made are given in Table 3.

1.2.2. Modification by cross linking

For membrane use, it has been already stated that the PVA based membranes have to be modified. Cross linking is one of the ways the properties of the basic polymer can be altered, especially capacity of the polymer for water uptake, degree of swelling, thermal, chemical and mechanical stability (brittleness) and its capacity to retain acid functionality (so called acid leaching) methodology adopted to impart proton conductivity. One of the ways of decreasing solubility in water is to increase cross linking, however, one has to be concerned with increased brittleness due to excessive cross linking and the level of swelling in the case of uncoiled situation. PVA can be cross linked in a variety of ways like freezing [15], heat treatment [16], irradiation [17] and chemical treatment [18]. Some typical examples are shown in Fig. 4. It may be realized that chemical modification has been preferred over physical modification for membrane applications.

1.2.2.1. Cross linked by irradiation. Irradiation has been conventionally employed as a means of modifying the polymers in addition to using them for the initiation and sustaining polymerization reaction. Adopting this methodology, PVA solutions have been irradiated by ^{60}Co gamma rays at room temperature at a dose rate of 0.5 kGy h^{-1} up to the integral radiation doses of 14 kGy for cross linking of 3% and 5% PVA solutions [19]. When PVA is irradiated in oxygen-free aqueous solution, the polymer radicals are formed indirectly induced mainly by the H^\bullet and OH^\bullet radicals arising from water molecules, both of which abstract the hydrogen atom(s) from the $-\text{CH}(\text{OH})-$ and/or $-\text{CH}_2-$ groups of PVA to form the polymer radicals. These polymer radicals may interact with one another by disproportion, and combination through inter- and/or intra-molecular cross linking, giving 3D polymer network [20,21].

1.2.2.2. Chemical cross linking. Variety of chemical reagents like sulfosuccinic acid, poly (acrylic acid), glutaraldehyde has been employed for cross linking PVA. For example, PVA has been cross-linked with varying amounts (5–30 wt.%) of sulfosuccinic acid (SSA), cast and heat treated at 393–403 K for 2 h (the possible structure of cross linked polymer is shown in Fig. 5). The proton conductivity and methanol permeability are dependent on the amount of sulfosuccinic acid content and the temperature employed for cross linking. The methanol permeabilities of the entire cross linked PVA/SSA membranes decrease until the amount of SSA reached around 15–17 wt.% and increase above this amount of SSA. This tendency becomes more distinct in the case of methanol permeability, depending on the cross linking temperature. This change in the methanol permeability over the amount of SSA and cross linking temperature may be regarded as two main



Fig. 2. Multi facets of PVA membrane.

Table 2
Properties of PVA based membrane.

Membrane	Dry thickness (μm)	Conductivity (Scm^{-1})	IEC (M equiv g^{-1})	Water uptake (%)	Methanol permeability ($\text{Cm}^2\text{s}^{-1} \times 10^{-6}$)	Ref
PVA/SSA	100–150	0.001–0.01	0.5–2.24	10–80	0.1–1	[5]
PVA/ sPTA	100–150	0.024–0.035	3.4	—	<1.8	[6]
PVA/sulfo acetic acid/ polyacrylic acid	125	0.00057–0.00192	0.092–0.654	1.84–62.48	0.00266–0.346	[7]
Poly(vinyl alcohol-co-2-methyl-1-propanesulfonic acid)/ GA	—	0.216	—	—	0.1	[10]
PVA-co-PE/IDA/PA	—	0.01	—	—	—	[11]
KOH containing PVAHEMA-SiO ₂	—	0.11	—	—	—	[12]
PVA/PSSA_MA/F	—	0.053	0.6–0.72	—	0.34–0.5	[13]
PVA/PAA/ UV radiation/	—	0.312	—	—	—	[14]
PVA/gamma irradiation/KOH	100–400	0.00006–0.013	—	—	—	[19]
PVA/EPTMAC/GA	—	0.0027420.00734	—	—	1.0–4.1	[21]
PVP/PVA-PAMPS	100	0.088	1.63	—	0.61	[26]
PVA/PSSA_MA	100–150	0.001–0.044	0.73–1.22	22–85	0.241	[27]
PVA/PSSA_MA/Silica	—	0.01–0.026	—	—	0.46–1.2	[28]
PVA/SSA/GA	—	0.01–0.0526	0.576–2.676	—	0.14–2.9	[29]
PVA/p-sulfonate phenolic resin	300–400	0.012–0.197	0.28–2.66	49.85–366.2	0.1	[30]
PVA / Nafion	181–201	0.0009–0.02	0.09–0.91	13–43	0.31–0.65	[33,34]
PVA/ Nafion/Chitosan	—	0.01	—	41–95	1.0–2.2	[35]
Nafion/PI/PVA/TSPS	—	0.063–0.064	—	16.8–22.5	0.489–0.7	[36]
PVA/PI/TSGEPS	90	0.01–0.04	—	—	0.14–0.432	[37]
PVA/PSSA	110	0.17–0.246	1.58	—	—	[39]
PVA/PSSA	150	0.0013–0.0166	1.9–2.6	—	—	[38,40]
PVA/PSSA/MOR	160	—	2.68–3.32	—	—	[41]
PVA/SSA/PSSA_MA-semi interpenetrating network	100–120	0.006–0.0259	1.1–1.86	20–60	0.09–0.4	[42,43]
PVA/PSSA-MA/GA	100–150	0.1	3.4	—	0.253	[44]
PVA/PAMPS/OG	60–100	0.06–0.1	—	<90	1/3–1/5 of Nafion-117	[45]
PVA/PAMPS/PEGBCME/ semi-IPN	60–70	0.095	1.79	3 fold of Nafion	1/3 of Nafion	[47]
PVA/Pvdf-HFP	160–190	0.085	—	—	—	[50]
PVA/SPEEK	—	—	0.47–0.72	—	3.5	[51]
PVA/SPEEK double layer	—	—	0.73–1.17	43–70	1.31	[52]
PVA/SSA/PVP	—	0.004–0.01	—	44–128	0.06–0.1	[54]
PVA/SA/GA	—	0.01	0.79	—	0.069	[55]
PVA/CS/GA	—	0.0099	0.62	—	0.094	[55]
PVA/APDPS/ Phosphonic acid	—	0.03–0.046	1.37–1.85	—	0.14–0.2	[63]
PVA/CS/ Organophospho-ric acids	107–110	0.02–0.03	0.75–1.33	52–79	0.23–0.42	[65]
PVA/KOH	80–100	0.002–0.004	—	36.1	—	[67]
PVA/PTSA	—	—	0.3–2.2	—	0.32	[66]
PVA/NH ₄ Br	—	0.005	—	—	—	[68]
PVA/ functionalized silica	200–300	0.03–0.2	—	—	—	[79]
PVA/ Phosphoric acid functionalized aminopropyl triethoxysilane	—	0.02–0.05	1.09–1.95	71–123	0.4–1.0	[80]
PVA/ AESP	200	0.03–0.07	1.21–1.76	55.6–80.9	0.2–0.6	[81]
PVA/TMAPS functionalized silica	20	0.031	—	—	—	[82]
PVA/Colloidal silica/ SSA	120	0.001	0.9–3.3	15–25	—	[83]
PVA/Phosphosilicate	80–200	0.02	—	—	—	[84]
PVA/FS/KOH	160–200	0.058–0.16	—	—	2.58–3.88	[85]
PVA/TiO ₂	100–200	0.0046–0.048	—	—	0.36	[86]
PVA/TiO ₂	100–300	0.005–0.012	—	83–95	—	[87]
PVA/HAP	100–300	0.025–0.044	—	45–60	—	[88,89]
PVA/PTA	150	0.03	—	—	—	[92]
PVA/PWA	80–100	0.006	—	—	0.1–0.4	[93]
PVA/PWA/SiO ₂	—	0.011–0.012	—	—	0.035–0.01	[94]
PVA/STA	90–110	0.0002–0.047	—	40	1.3	[98]
PVACO/PMA	90–110	0.000–0.002	—	—	1.5–3.9	[99]
PVA/Zirconium phosphate	—	0.01–0.03	3–3.2	140–260	2–3.5	[101]
PVA/MMT	100–300	0.0368	—	—	3–4	[107,108]
PVA/ntTiO ₂ /PSSA	100–200	0.001–0.002	—	—	0.3–0.8	[111]
PVA/ Organo clay/PSSA_MA	—	0.023	0.79–1.68	—	0.2	[112]
PVA/NCBC/Silica	—	0.019–0.053	1.4–1.73	—	0.2–1	[113]
PVA/sPOSS/EDTAD	—	0.042	0.3–0.8	130–135	0.18	[114]
PVA/SiO ₂ /SSA	—	0.001–0.01	0.2–1.1	45–60	0.01–0.1	[115]
P-PVA/PEG-SiO ₂	100	0.0017	—	—	—	[118]
PVA/PAA/Silica	—	0.001–0.01	0.46–1.58	30–55	0.01–0.1	[116]
PVA/SPEEK/PWA	—	0.001	1.3–3.6	—	—	[117]
PVA/SSA/ Sulfonated Benzene-silica Hybrid membrane	—	0.039	0.08–0.6	—	0.5	[119]

factors. Namely, one is the cross linking effect of the PVA matrix by adding SSA and the other is the effect of hydrophilicity introduced by the $-\text{SO}_3\text{H}$ groups. The cross linking of the PVA membranes by

the SSA to some extent say up to 17 wt% might cause increased accessible free volume, into which the methanol can permeate and retained and thus accounts to the reduced transport of methanol

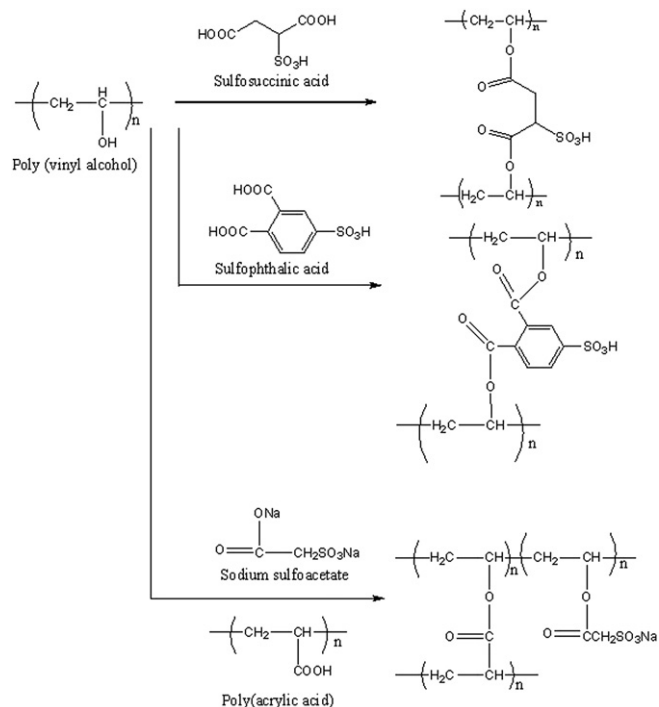


Fig. 3. Modification of PVA.

across this level of cross linked PVA membranes. Above this level of cross linking probably the accessible free volume is reduced and hence the methanol permeability also increases [5]. It is demonstrated that the DMFC with cross linked PVA/SSA solid polymer membrane shows excellent electrochemical performance at ambient temperatures and pressures. The maximum peak power density of the DMFC is about 4.13 mW cm^{-2} at 60°C and $1.01 \times 10^5 \text{ Nm}^{-2}$ [22]. PVA has also been crosslinked with poly (acrylic acid) by heat treatment at 423 K for 1 h . PVA/PAA membranes have been used for the pervaporization separation of MTBE/MeOH mixtures [23]. The cross linking of PVA with glutaraldehyde has also been reported (basic unit of the polymer is shown in Fig. 6) [24]. Polyvinyl alcohol grafted with quaternary ammonium group has been crosslinked with glutaraldehyde (the

Table 3

Brief summary of the methodology used for the modification of PVA.

S.No	Co agents employed	Property variation observed	Ref
1	Addition of 2 or 4% of 2-methyl-1-propanesulfonic acid (AMPS)	Proton conductivity shows a relationship to the concentration of AMPS	[10]
2	Copolymerizing with ethylene with 4,5 imidazole dicarboxylic acid (IDA)	Membrane swelling property and mechanical property	[11]
3	Copolymerizing with ethylene in presence of IDA and phosphoric acid (PA)	Proton conductivity is a function of temperature and content of IDA/PA	[11]
4	Copolymerizing with 2-hydroxy ethyl methacrylate (HEMA) and UV irradiation - PVAHEMA-SiO ₂ in 40% KOH	Ionic conductivity increases	[12]
5	Surface fluorination of the copolymer with Poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA)	Increase of proton conductivity and decreased methanol permeability	[13]
6	PVA/Poly(acrylic acid)(PAA)	Crystallinity decreases and ionic conductivity increases	[14]

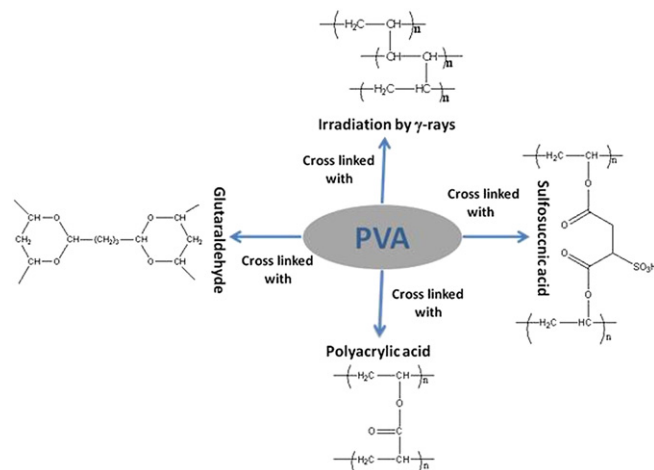


Fig. 4. Cross linked PVA.

structure of the basic building unit is shown in Fig. 7). These membranes show proton conductivity in the range of $(2.74\text{--}7.34) \times 10^{-3} \text{ S cm}^{-1}$ in deionized water at room temperature. It is also reported that the ionic conductivity decreases with increasing degree of cross linking. With the addition of the cross linker, the structure of the membranes becomes compact, and the anion transferring channels becomes narrower. At the same time, the water content in the membrane decreases. Hence, the activation energy for the ion transport through the membrane increases and the ionic conductivity of the membrane decreases with increasing degree of cross linking [25].

PVA is chemically cross linked with 2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS) and poly(vinylpyrrolidone) (PVP) for low temperature direct methanol fuel cell applications [26]. Membrane swelling decreases with time of cross linking, accompanied by an improvement in mechanical properties and a small decrease in proton conductivity due to the reduced water absorption. The membranes attain a value of 0.088 S cm^{-1} for proton conductivity and $1.63 \text{ M equiv g}^{-1}$ of IEC at $298 \pm 2 \text{ K}$ for a polymer composition PVA–PAMPS–PVP being 1:1:0.5 in mass. This system though showed comparable proton conductivity to Nafion 117, showed a methanol permeability of $6.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is only one third of Nafion 117 methanol permeability under the same measuring conditions. The membranes display a relatively high oxidative stability without weight loss of the membranes. PVP, as a modifier, is found to play a crucial role in improving the performance of the membrane [26].

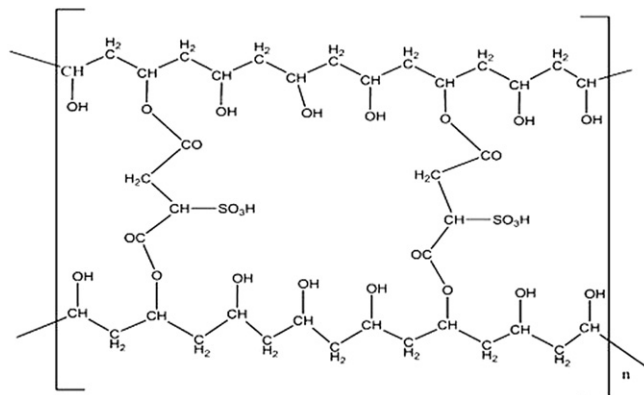


Fig. 5. Possible cross linking structure of PVA and SSA.

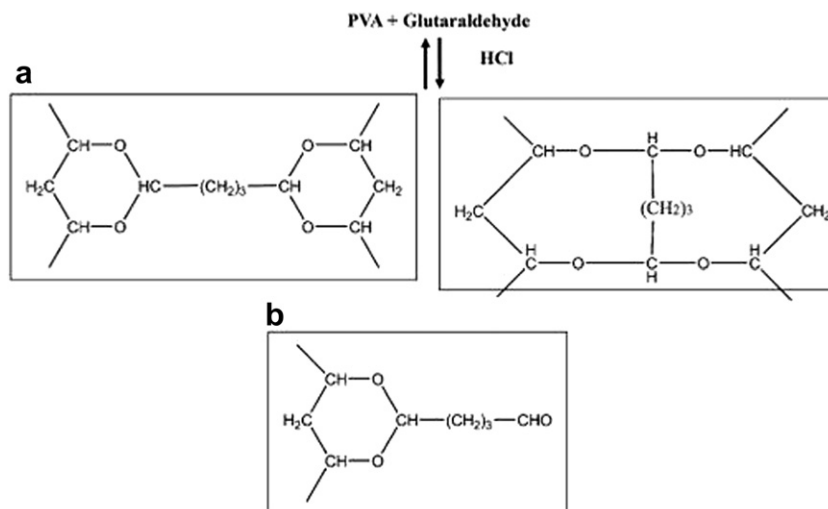


Fig. 6. Possible cross linking PVA formed by reaction between PVA and GA: (a) acetal ring group or ether linkage and (b) aldehyde formation by monofunctional reaction.

PVA can also be crosslinked effectively using poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA) to give membranes useful in the DMFC. The PSSA-MA is used both as a cross linking agent and as a donor of the hydrophilic- SO_3H and/or- COOH groups [27,28]. Recently it has been reported [29] that PVA is crosslinked with double cross linking agent involving two step processes (one such example using sulfosuccinic acid and glutaraldehyde is shown in Fig. 8). It uses sulfosuccinic acid (SSA) as the first cross linking agent to form an inter-crosslinked structure and then as a promoting sulfonating agent. Glutaraldehyde (GA) as the second cross linking agent reacts with the remaining OH groups of PVA and forms, not only a dense structure at the outer membrane surface, but also a hydrophobic protective layer. The membranes prepared by the two-step cross linking process exhibit excellent dissolution resistance in water compared with membranes prepared by a traditional one-step cross linking process. The membranes become water insoluble even at a molar ratio of $\text{SO}_3\text{H}/\text{PVA-OH}$ as high as 0.45. Moreover, the synthesized membranes also exhibit high proton conductivities and high resistance for methanol permeability. The currently available literature reports highest proton conductivity of $5.3 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature from one of the synthesized membranes, higher than that of the Nafion[®] membrane. Methanol permeability of the synthesized membranes is in the range of $1 \times 10^{-7} \text{ cm}^2 \text{ S}^{-1}$, which is about one order of magnitude lower than that of the Nafion[®] membrane [29].

1.2.3. Modification by blending

Chemical modification by sulfonation may induce the desired characteristics like conductivity, it may adversely affect the

mechanical properties of the polymer formed. Blending of sulfonated proton-conducting polymers with PVA polymers is another approach to separately achieve the requirements for high proton conductivity on one hand and good mechanical properties on the other. PVA has been blended with a variety of sulfonated polymers like SPEEK, Nafion, PSSA and PSSA-MA. Membranes composed of poly (vinyl alcohol) (PVA) and a proton source polymer, sulfonated phenolic resin (s-Ph) have displayed good proton conductivity of the order of $10^{-2} \text{ S cm}^{-1}$ at ambient temperatures [30]. In this blended polymer, the proton is shared between the sulfonate group and the hydroxyl (weak base) of PVA forming hydrogen bonded network, the acid–base pairing can lead to short range ordered domains thus creating a directional proton flow channel. Specifically in the present case, a covalent bond is formed between the s-Ph and PVA moiety when the blend is dehydrated at elevated temperatures. This increases the membrane strength. In addition, the membrane shows decreased solvent uptake and reduced swelling with increasing methanol concentration, which is advantageous for the application in direct methanol fuel cells (DMFC) [30]. The membrane consisting of blended polymer with sulfonated poly (ether ether ketone) and sulfated poly(vinyl alcohol) is reported [31]. This membrane showed an increase in resistance to methanol transport with increased sulfonation content in the blended polymer especially at high methanol concentrations.

A modified membrane structure consisting of the native Nafion membrane coated on both sides by the recast layer of PVA and Nafion mixture has been reported [32]. Further improvement in mechanical strength and protonic conductivity of the membrane can be achieved by subsequent steps of chemical cross-linkage and sulfonation. This membrane demonstrates a good selectivity for water over methanol. A Nafion[®]/PVA blend membrane at 5 wt% PVA (annealed at 503 K) results in a similar proton conductivity to that of Nafion[®] 117 and a methanol permeability three times lower than that of Nafion[®] 117 [33]. As PVA content increases in the blend membranes, the proton conductivity decreases to values lower than that of Nafion[®] 117, however, an unusual trend is observed in a Nafion[®]/PVA blend membrane at 50 wt% PVA, where proton conductivity remains relatively constant, but methanol permeability decreases by one order of magnitude with increasing annealing temperature. This trend differs from most investigations, where proton and methanol transport usually increase or decrease

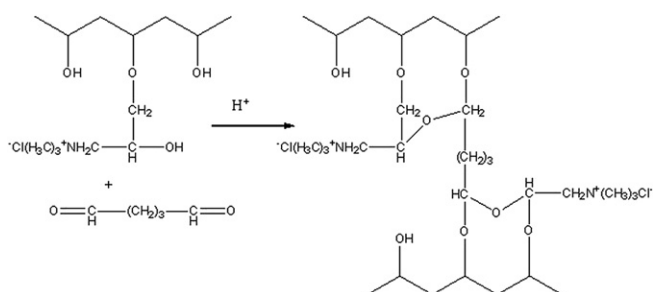


Fig. 7. The cross linking of QAPVA.

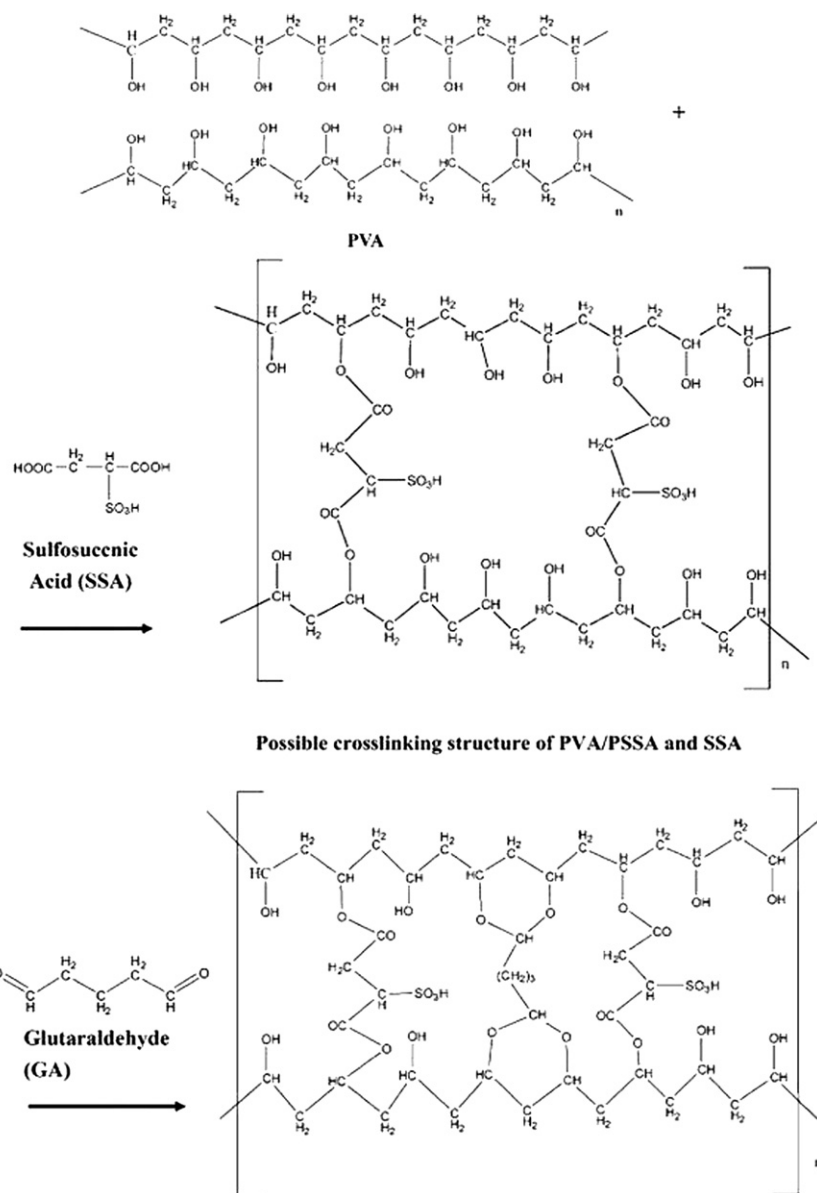


Fig. 8. Possible structure of the PVA-SSA-GA membrane by two step cross linking [29].

simultaneously in sulfonic acid containing PEMs with changes in polymer properties (e.g., ion content, water content, morphology). The results of this study show that the two phenomena namely the proton and methanol transport can be decoupled. It is also suggested that this unusual trend occurs due to changes in the phase behavior of the blend at different annealing temperatures [34]. A series of cost-effective, proton-conducting composite membranes, comprising of Nafion[®] ionomer, chitosan (CS), and polyvinyl alcohol (PVA), is reported [35]. By taking advantage of the strong electrostatic interactions between the polyanion Nafion[®] and polycation CS component, Nafion ionomer is effectively implanted into the PVA/CS composite membranes, thus improving the proton conductivity of the PVA/CS composite membranes. Furthermore, this effect depends on the composition ratio of PVA/CS, and the optimum conductivity is obtained at the PVA/CS ratio of 1:1. The developed composite membranes exhibit lower methanol permeability compared with the widely used Nafion[®] membrane. Blending of polymers can decrease the transport of methanol,

however, a reduction of methanol permeability is always accompanied by a significant reduction in proton conductivity. Therefore, they fail to meet the requirement of durability under DMFC operating conditions. To overcome this drawback, preparation of composite membranes using Nafion115 membrane modified with polyvinyl alcohol (PVA), polyimide (PI) and 8-trimethoxysilylpropyl glycerin ether-1,3,6-pyrenetrisulfonic acid (TSPS) (Fig. 9) has been attempted since they combine the attractive features of each component [36]. Polyimide and PVA decrease the methanol crossover. Besides, PI possesses excellent thermal stability and mechanical strength. 8-trimethoxysilylpropyl glycerin ether-1,3,6-pyrenetrisulfonic acid (TSPS) not only provides a large amount of proton, but also forms a cross-link network with the base material to avoid its weight loss in water. The proton conductivity of Nafion/PI-PVA-TSPS is slightly decreased by 1–3% compared with Nafion115. Especially, the addition of organic proton conductor (TSPS) compensates for the decrease in proton conductivity of membranes when non-sulfonated nanofillers are utilized.

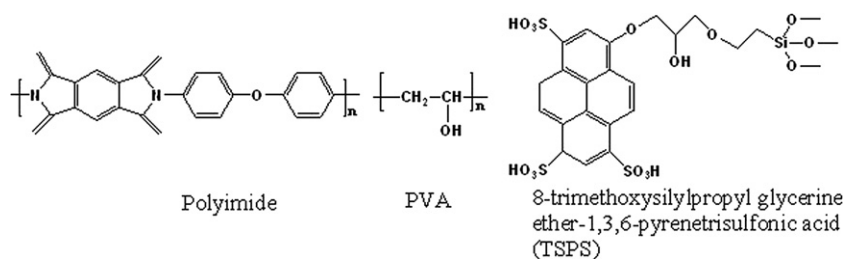


Fig. 9. Structure of modification for the composite membranes.

Furthermore, it avoids the sulfonic acid group to directly link with the main chain of the polymer that leads to the polymer degradation. The methanol permeability of Nafion/PI–PVA–TSPS composite membranes is remarkably reduced by 35–55% compared with Nafion115. The lower methanol permeability of the composite membranes is consistent with their lower water uptake. This phenomenon can be mainly attributed to two reasons: (1) PI and PVA have high resistance to methanol crossover, and (2) the silica of TSPS formed by a sol–gel reaction increase the length of the transport path along which methanol permeates through the membrane [37]. It has been demonstrated that PVA–PSSA blend is a potential proton-conducting membrane with lower methanol crossover in relation to Nafion-117 membrane [38]. Polymer blends of PVA and PSSA have been developed by a sol–gel route with varying PSSA content [39]. Interestingly, the PVA and PSSA membrane exhibits higher water uptake and release characteristics in relation to both pristine PVA and Nafion® membranes. These membranes generally display comparable or superior proton conductivity with respect to Nafion although, they are soluble in water. This work demonstrates the concept of “TPL membrane” as a viable method to make stable membranes with ion conduction characteristics. Since this method is amenable for preparation in a variety of ways, and materials, it is possible to engineer the properties of the membrane [40]. Membranes with mordenite (MOR) incorporated in PVA–polystyrene sulfonic acid (PSSA) blend tailored with varying degrees of sulfonation have been reported [41]. Such a membrane comprises of a dispersed phase of mordenite and a continuous phase of the polymer that help tuning the flow of methanol and water across it. Mordenite, a proton-conducting methanol impermeable zeolite with regular pore sizes provides selective separation of molecules based on their size and shape. Mordenite also helps in separating components on the basis of preferential adsorption where the strong adsorption of one component blocks or hinders the phases of the other components. A peak power density of 74 mW cm^{-2} is achieved for the DMFC using a PVA–PSSA membrane electrolyte with 50% degree of sulfonation and 10 wt. % dispersed mordenite phase [41].

It has been reported [42] that the PVA/PSSA-MA membranes exhibit excellent electrochemical properties for electro-dialytic separation. A series of semi-interpenetrating network (SIPN) membranes was synthesized by using poly(vinyl alcohol) with sulfosuccinic acid (SSA) and poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA) and their physio-chemical and electrochemical characterizations have been reported (a schematic network structure for this polymer blend is given in Fig. 10) [43]. The semi-IPN membranes with PSSA-MA over 60% exhibit higher proton conductivity than Nafion-115 and also a reasonable level of water uptake. Highly efficient proton-exchange membranes (PEMs) have been made by using polymer blends of water soluble PVA and poly(styrene sulfonic acid-co-maleic acid) (i.e. PVA/PSSA-MA) [44]. A maleic acid group has two ion-exchangeable sites in a molecular unit and also exhibits the lower water uptake than that of the

sulfonic acid group. The introduction of maleic acid into PSSA can significantly increase the charge density in the membrane and also prevent excessive swelling. Upon successive thermal and chemical treatments of the membranes, the methanol permeability decreases more than one order of magnitude compared with Nafion 117 but the proton conductivity is as high as 0.1 S cm^{-1} at room temperature. During the thermal treatment, the hydrogen bonds between hydroxyl groups of PVA and sulfonic or carboxylic groups of PSSA-MA are possibly formed. This physical interaction between the functional groups results in the formation of hydrophilic ionic channels or micro-domains by the arrangement of hydrophilic polymeric groups. During the chemical treatment, alcohol groups of PVA matrix can be crosslinked with glutaraldehyde (GA) which, with its increased hydrophobic character can function as methanol barrier to provide the polymer with the morphological stability and to prevent the polymer from dissolving in solvent. This structural feature is responsible for the reduction of methanol permeability through the membranes [44].

A different type of proton-conducting membrane based on PVA–PAMPS has been reported [45]. In particular, greater hydrophilicity of the membranes emerged, which endows them with excellent oxidative stability. It is considered that the membrane microphase structure is improved with incorporation of HMw-PVA. To improve the properties of PVA/PAMPS membrane, PVA/PAMPS blends based semi-IPN by incorporating plasticizer variants R (R = poly(ethylene glycol)(PEG), poly(ethylene glycol) methyl ether (PEGME), poly(ethylene glycol) dimethyl ether (PEGDE), poly(ethylene glycol) diglycidyl ether (PEGDCE)) and poly(ethylene glycol) bis(carboxymethyl)ether (PEGBCME) as the third component [46–49] have been synthesized. These blends showed high proton conductivity (0.1 S cm^{-1}), flexibility with low methanol permeability ($1/3$ – $1/2$ of Nafion membrane), and also excellent hydrolytic and the oxidative stability. Incorporating poly (ethylene glycol)bis(carboxymethyl) ether (PEGBCME), a double carboxylic acid end group in PVA/PAMPS contributes to the high proton conduction of the membranes in addition to the sulfonic acid groups in PAMPS (the building unit and a typical morphology are shown in Fig. 11). The

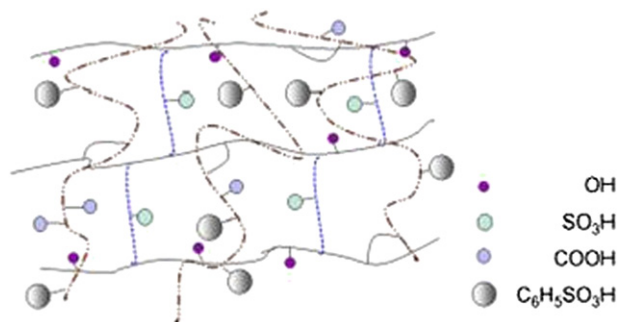


Fig. 10. The SIPN structural scheme of PVA/SSA/PSSA-MA membrane [42].

water uptake of the membranes decreases due to the further cross linking between the—COOH of PEGBCME and the—OH of PVA, which is responsible for the good longevity of MEA in DMFC. PVA–PAMPS–PEGBCME is a fully hydrocarbon based membrane made up of simple aliphatic skeletons. Among the various polymers for blending with PVA, PVdF–HEF attracts the researcher for its concurrent crystalline and amorphous natures, in which the amorphous phase promotes the ionic conductivity and crystalline nature accounts for increased mechanical strength of the membrane.

Factors like high dielectric constant and glass transition temperature also influence the application of PVA membrane in fuel cells. Phase inversion technique is employed to prepare porous PVdF–HFP/PVA membranes and the pores are filled with aqueous highly concentrated acid solutions such as H_3PO_4 and H_2SO_4 . The membrane exhibits high ionic conductivity and thermal stability. The higher ionic conductivity of the porous PVdF–HFP electrolyte membrane is attributed to the extended porosity and acid uptake of the network. Increase of amorphous nature facilitates the flexibility of the polymeric backbone [50]. The study of SPEEK/PVA blend membranes has been considered to be one of the alternatives, which offers the attribute of adjustable proton conductivity, excellent chemical and thermal stability [51]. Detailed studies of blend membrane on uptake of water from methanol solution showed that PVA can reduce the absorption in methanol solution. The opposite influences of PVA at different liquid environments as compared to pure water are favorable for DMFC applications, which can reduce the swelling of membranes and maintain the tight contact between electrolyte membrane and catalyst. Proton conductivities of blend membranes are slightly lower than those of the pure SPEEK membrane. The low methanol permeability of the blend membranes shows good potential for usage in DMFC [52]. It has been reported that the PVP polymer employed in the membranes can efficiently improve the oxidative stability and mechanical properties of the membranes [26]. Another study reports the exceptional water or methanol sorption selectivity of poly (vinyl alcohol)/poly (vinyl pyrrolidone) blends [53], however, an excessive swelling usually exists in PVA/PVP based membranes. To reduce the excessive swelling, a semi-interpenetrating (SIPN) structure based on a cross linked PVA/SSA network and penetrating PVP molecular chains has been prepared. The membrane with 20 wt% PVP (SIPN-20) exhibits a proton conductivity value comparable to that of Nafion® 115 ($1.0 \times 10^{-2} \text{ S cm}^{-1}$ for SIPN-20 and $1.4 \times 10^{-2} \text{ S cm}^{-1}$ for Nafion® 115). SIPN membranes are known to reveal excellent methanol resistance for both sorption and transport properties. Methanol uptake in a SIPN-20 membrane is only half that of Nafion® 115. Accordingly, SIPN membrane with a suitable PVP content is considered as a good methanol barrier (the network unit responsible for this is shown in Fig. 12) [54]. Membranes made of poly (vinyl alcohol) (PVA) and its ionic blends with sodium alginate (SA) and chitosan are reported [55,56]. The addition of small amounts of anionic polymer is particularly instrumental in the significant reduction of methanol transport.

1.2.4. Modification by acid–base

1.2.4.1. Acid doped PVA. Acid base properties of the membranes and hence hydrophilicity of the membranes can be modulated using mineral acids. An approach to eliminate water dependence for sulfonic acid membranes is to use phosphoric acid as proton conductors. The water binding energy of phosphonic acid (47.3 kJ mol^{-1}) is found to be higher than that of sulfonic acid (44.4 kJ mol^{-1}) [57], suggesting that the phosphonic acid group has a better capacity of retaining water under low-humidity conditions and that the dynamics of the hydrogen bonding is more constrained with— PO_3H_2 than with— SO_3H . The proton transport

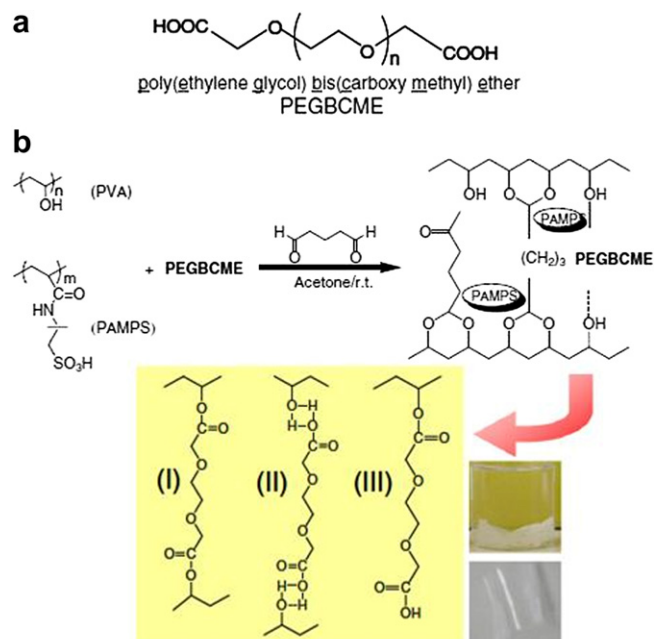


Fig. 11. (a) Chemical structure of novel plasticizer PEGBCME and (b) PVA–PAMPS–PEGBCME semi-IPN [47].

through membranes containing phosphonic acid under low-humidity conditions is carried out via diffusion along hydrogen bonds [58,59]. The average (zero point energy (ZPE) corrected) energy for phosphonic acid and sulfonic acid is 37.2 and 69.9 kJ mol^{-1} , respectively, indicating that protons transport is easier from ‘acid to acid’ via phosphonic acid groups than via sulfonic acid groups [57]. Hence, the proton conductivity can be significantly increased after doping with H_3PO_4 [60] and other heteropolyacids [61,62]. However, a leaching of the inorganic acids from the membrane, especially when contacted with liquid fuels, often occurs for these acid-doped membranes. The leaching of acids results in a fast decrease of conductivity. It can also cause corrosion problems. In order to address this problem, synthesis of phosphonic acid membranes through chemical modifications of polymers has been introduced (the sequence of steps adopted in this methodology is shown in Fig. 13) [63]. Proton conductivity of phosphonic acid membranes is directly associated with the degree of phosphonation. The presence of higher density of phosphonic

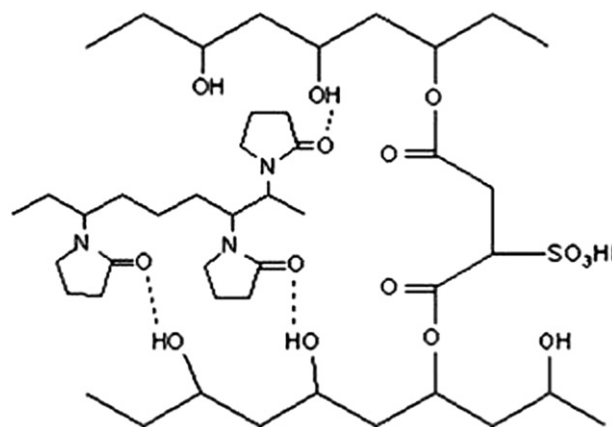


Fig. 12. The SIPN structural scheme of the PVA/SSA/PVP membrane.

acid groups in the membrane gives rise to higher proton conductivity [64]. The disadvantages of the relatively complicated procedure for fabrication of chemically modified membranes and the leaching problem for physical doping membranes promote the development of incorporation of organophosphorus acids (OPAs) into alcohol barrier materials (polyvinyl alcohol/chitosan, PVA/CS) (Fig. 14) to simultaneously acquire high proton conductivity and low methanol permeability [65]. Novel acid base membrane composed of p-TSA as an acidic compound and PVA as a basic compound have been prepared with glutaraldehyde (GLA) as a cross linking agent. The crystallinity of the host polymer is disrupted by the addition of pTSA and GLA. This influences the flexibility of the polymeric back bone. The cross linking agent GLA ensures the required thermal and mechanical stability of the prepared membranes. The hydrophilic nature of the polymer enhances due to the inclusion of pTSA content which favors the ion migration [66]. Most of these acid-doped polymers exhibit proton conductivity less than $10^{-3} \text{ S cm}^{-1}$ at room temperature. High acid contents result in high conductivity but lower mechanical stability, especially at temperatures above 350 K.

1.2.4.2. Alkali doped PVA. Alkali doped PVA membranes are transparent and homogeneous with mechanical flexibility. When immersed in KOH solutions, the PVA membrane becomes orange in color but it becomes almost colourless by rinsing the membrane in deionized water. The chemical interaction, such as dipole–dipole interaction including hydrogen bonding and induction forces, may operate between CO and OH groups of PVA and KOH during alkali doping, which is useful for the ionic conductivity of PVA. However, the ionic conductivity decreases with increased

concentration of the doping agent namely KOH, for example, when KOH concentration in solution is larger than 4 M, the resulting membrane shows decreased conductivity. The membrane samples are found to be supernatant at high concentrations of KOH ($>8 \text{ M}$) in solution. It appears that more OH^- could not be included into the polymer at high KOH concentration due to decreased ionic mobility caused by ion pair formation or due to increased viscosity of the solution [67]. PVA-based polymer electrolytes with different compositions of ammonium bromide have been prepared using the solution-casting technique. The maximum conductivity value ($5.7 \times 10^{-4} \text{ S cm}^{-1}$) is obtained for the polymer complex with 25 mol% NH_4Br [68].

1.3. Composites with PVA

1.3.1. Inorganic organic composite membrane

One of the main approaches taken to improve the performance of PVA membranes is the formation of composite membranes. Both organic–inorganic composites (which reduce methanol crossover) and acidic–basic composites (which reduce methanol crossover and increase conductivity) have been investigated. The inclusion of ceramic materials, such as Al_2O_3 , TiO_2 or SiO_2 , into a polymer matrix has two objectives: one is to improve the mechanical properties of the membrane; the other is to physically counteract methanol crossover. It is suggested that inorganic oxides enhance the ionic conductivity of the membrane, however, a number of studies made on this issue reveal some discrepancies. The size of the particles (nano or micro), their surface properties (acidic or basic) and their functionalization determine whether the filler material, besides acting as a reinforcing component, also imparts

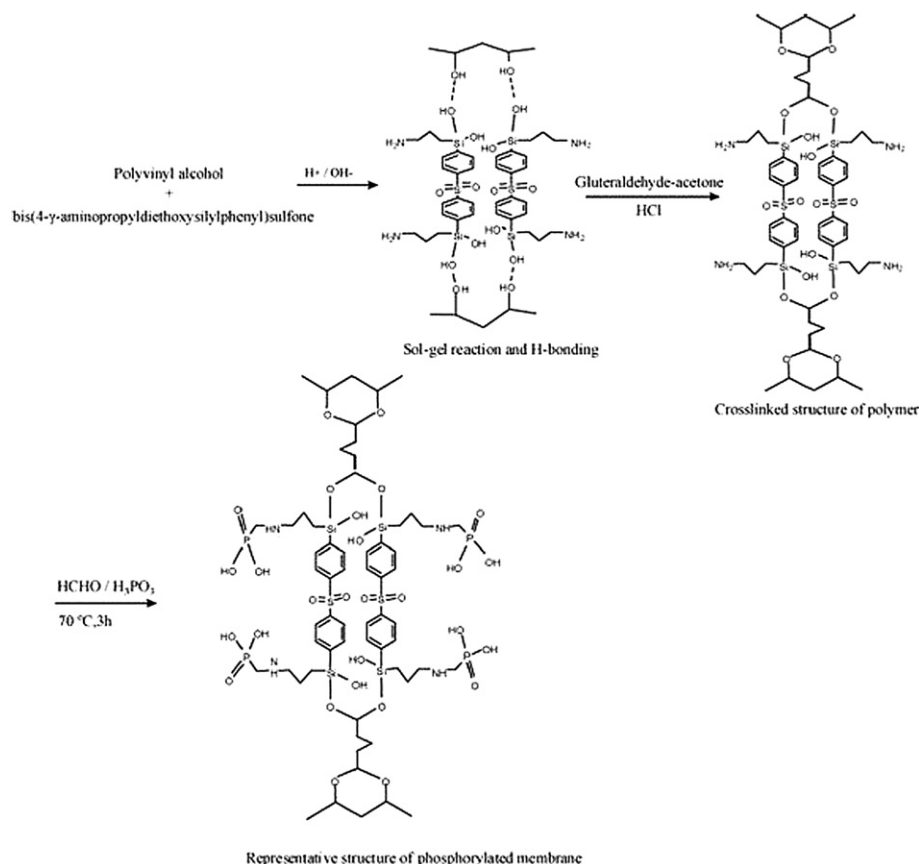


Fig. 13. Schematic reaction route for membrane preparation [63].

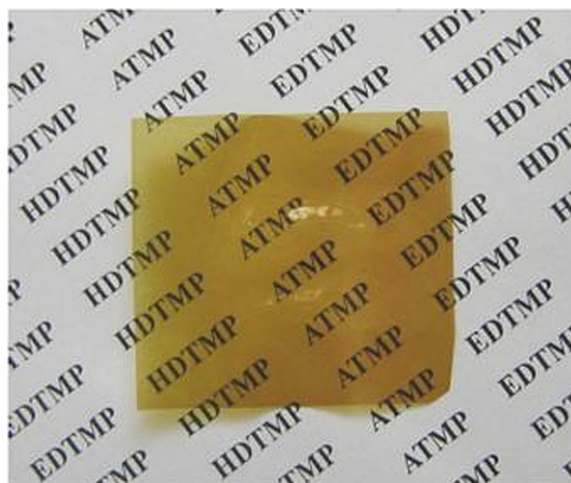


Fig. 14. A representative photograph of the OPA-doped PVA/CS blend membranes [65].

a significant improvement in ion conduction. In the latter case, it is not completely clear whether the ceramic filler actively participates in the ion conduction by enhancing ion dissociation or by providing favorable pathways for the ion transport along polymer–ceramic interface. There are also other open questions concerning the impact of the ceramic filler on morphology. Depending on the particular polymer–ceramic filler combination, amorphous or crystalline phases might be promoted.

An effective way to achieve low humidity and high temperature operation is to cast polymers with fillers like silica, alumina, Zirconia, titania, tungsten trioxide, aluminium oxy hydroxide and tin oxide and other solid acids like heteropolyacids [1,69–72] which are hygroscopic in nature. The original concept was proposed by Watanabe et al. [73], which formed the base for the development of self-humidifying composite membranes. Such hygroscopic oxides have also been incorporated into PVA [70,74].

It has been shown that the water uptake by the oxide containing membrane is higher than that of the pristine polymer. Composite membranes with hygroscopic oxide exhibit improved thermal and mechanical stability than the parent polymer. They all, in common exhibit reduced methanol permeability. The addition of hygroscopic oxide results in change in structure of membrane, where the particles block part of the hydrophilic polymer channels through which protons migrate. (See Fig. 15) [75]. Narrowing water

channels allows low solvent penetration and electro osmotic-drag coefficient. Discussion on some of the typical hybrid systems based on PVA and inorganic species is given below.

1.3.1.1. PVA/ silica. Modification of PVA through the addition of silica is a common approach utilized for the improvement of membrane performance in DMFC applications. PVA-silica membranes have been prepared according to several methods by casting mixtures such as: silica powder, sol–gel reaction followed by solution casting of the PVA solution. Mixed matrix membranes (MMMs) containing PVA and 10–30 wt% fumed silica (FS) have been prepared using a solvent casting method [76]. This study has aimed to create physical cross linking by incorporating FS nanoparticles into PVA. The surface roughness of the membrane increases with higher FS content whereas membrane crystallinity decreases with increase in FS content. This is due to the fact that the FS particles will restrict the polymer chain mobility. The confined chain mobility inhibits crystal unfolding and thus suppresses the dissolution of the membrane in water. This finding is confirmed by the enhanced crystallinity of the swollen membranes with FS addition. The incorporation of FS has improved the thermal stability and resistance to dissolution in water, while decreasing the mechanical strength [77].

The effect of a functionalized silica filler, having a $\text{—SO}_3\text{H}$ end-group, on cross linked PVA membranes has been reported [78,79]. The thermal analyses have demonstrated the role of the inorganic compound in improving the stability of the membranes and in reducing the crystalline phase of the polymer matrix. In addition, silica particles have a positive effect on the retention of the absorbed liquid phase i.e. water since these molecules are supposed to coordinate to the functional group of the filler. Chain ordering is promoted by the presence of functionalized silica (SiO_x), whereas it is reduced upon cross linking with glutaraldehyde [79]. The development of proton-exchange membranes via sol–gel procedures in aqueous media may provide a more environment friendly and cost-effective process for membrane preparation since the use of harmful organic solvents can be minimized and also the process is relatively simple [80].

PVA/silica composite proton-exchange membranes were prepared by a sol–gel process in acidic conditions using amino propyl triethoxysilane as an inorganic precursor and functionalized with phosphonic acid. It is observed that an increase in the silica content in the membrane phase leads to a substantial increment in the water uptake of the membrane. This may be attributed to the increase of the functional groups because it is proportional to the

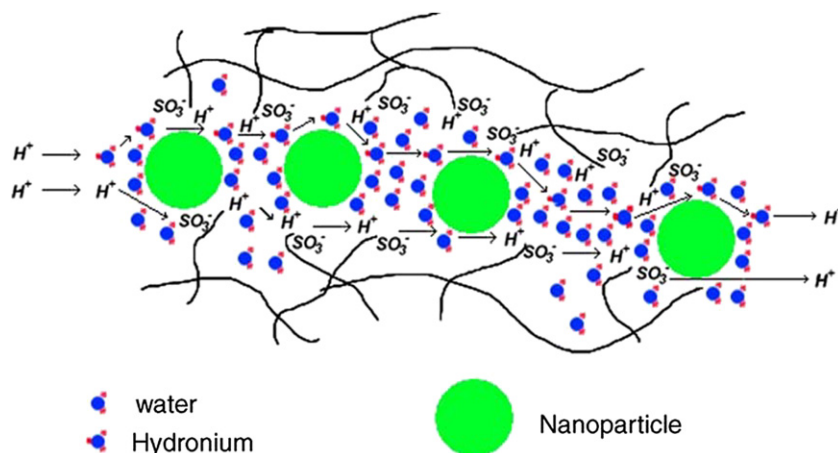


Fig. 15. Proton transport in hybrid membranes [75].

silica content on which PO_3H_2 groups were introduced. The hydrogen bonding between $-\text{OH}$ groups of PVA and $-\text{PO}_3\text{H}_2$ groups is expected due to the decrease in the distance between polymer chains. This physical interaction between functional groups leads to the formation of hydrophilic proton pathways or micro-domains which will function as a hydrophobic methanol barrier as well as providing morphological and structural stability to the polymer membrane [80]. Hybrid anion-exchange membrane with anion-exchange silica precursor (AESP) and PVA by sol–gel method in aqueous media has been reported (Fig. 16) [81]. Membrane properties are highly dependent on AESP content in the membrane matrix. It is observed that incorporation of AESP in the membrane matrix, improved their thermal stability (up to 530 K in dry nitrogen atmosphere). Quaternary ammonium group ($-\text{N}^+(\text{CH}_3)_3$) containing SiO_2 particles (TMAPS) is proposed to fill in PVA matrix. TMAPS not only functions as quaternary ammonium group, but also as silica donors. In addition, SiO_2 contained in TMAPS improves the thermal stability of composite membranes. Poly (vinyl alcohol)/3-(trimethylammonium) propylfunctionalized silica (PVA/TMAPS) was prepared by a simple solution-casting method. The thermal stability of the PVA/TMAPS membrane increases with an increase in the TMAPS content. The membrane with a weight ratio of PVA:TMAPS=90:10 have exhibited the highest OH^- ion conductivity of 0.031 S cm^{-1} in 3.0 M KOH solution at 298 K [82]. Modification of PVA membranes by incorporation of colloidal silicon leads to appreciable improvement of the proton conduction of membranes but it reduces mechanical properties after heat treatment. Reduction in mechanical properties of membrane is still in acceptable level, but some improvements may be necessary in order to ensure a sufficiently long membrane service life [83]. Composite membranes can be prepared by dispersing a colloidal suspension of solid particles into a polymeric matrix. Membranes were cast by mixing a phosphosilicate colloidal solution ($\text{P}_2\text{O}_5\text{--SiO}_2$) derived from a functionalized sol–gel process with a PVA solution [84]. This process begins with the colloidal suspension of solid particles. It

acts as a promising approach to provide a high degree and homogeneous dispersion of functional phosphosilicate gel particles into a polymer matrix in order to avoid the aggregation of solid particles. The synthesized composite membranes are extremely flexible. A large amount of functionalized phosphorous groups in the composite membrane allows for protons hopping to dominating proton conduction while diffusion transport of protonic ions is favored by the PVA polymeric domains [84]. Membranes formed by trapping highly conducting acid solutions in a PVA with grafted silica inside the polymer matrix have revealed an improvement in protonic conductivity [85].

1.3.1.2. PVA/titania. Titania is used in the form of nanoparticles with high surface area, activity and excellent chemical stability. The addition of hydrophilic nanocrystalline titanium oxide (TiO_2) filler into the polymer matrix serves to reduce the glass transition temperature (T_g) and the crystallinity of the PVA polymer and increases the amorphous phases of the polymer matrix, as well as increases its ionic conductivity. When the TiO_2 filler used as a stiffer material is added to the PVA matrix, the swelling ratio of the PVA/ TiO_2 composite polymer membrane is effectively reduced. Further, the thermal property, dimensional stability and long-term cycle life can also be improved. The nano-sized TiO_2 ceramic fillers are dispersed into the PVA matrix to act as a solid plasticizer capable of enhancing the chemical and thermal properties, as well as the dimension stability of the PVA/ TiO_2 composite polymer membrane [86]. The hydrophilic PVA polymer and the TiO_2 fillers prove to be homogeneous and compatible without any phase separation occurring when a suitable amount of TiO_2 ceramic filler was added. These cross linked PVA/ TiO_2 composite polymer membranes appear to be potential candidates for the DMFC applications [87].

1.3.1.3. PVA/HAP. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP) has long been used as an implant material due to excellent biocompatibility, bioactivity and chemical stability. Experimental results have indicated improvements in the ionic conductivity, thermal property, and dimension stability as different amounts of the ceramic fillers are added into the solid polymer electrolyte (SPE). The reason for the increase in the ionic conductivity of composite polymer electrolyte is explained that the ceramic particle fillers in the polymer matrix have created some defects and free volume at interface of the ceramic particles and the polymer chain. A composite polymer membrane based on poly (vinyl alcohol)/hydroxyapatite (PVA/HAP) was prepared by a solution casting method. The results have demonstrated that alkaline air-breathing DMFC with the PVA/HAP composite polymer membrane shows good electrochemical performances at ambient temperatures and pressure. The maximum peak power density of the DMFC is 11.48 mW cm^{-2} at ambient air and temperature. Thus it appears that the composite membranes will have potential for application in DMFC [88,89].

1.3.1.4. PVA/HPA. The heteropoly acids (HPAs), which are generally clusters of tungsten, molybdenum, or more rarely vanadium or uranium oxides, are a subset of a large class of inorganic oxides called the polyoxometallates (POMs) [90]. The HPAs distinguish themselves from other POMs in that they have a central heteroatom surrounded by a number of tungsten or molybdenum-oxygen octahedra. The HPAs are known to have high proton conductivity at room temperature, ($\sim 0.1 \text{ S cm}^{-1}$) where they are usually hydrated with ca. 20–29 water molecules per anion. At higher temperatures the conductivity usually falls even though the measured self diffusion coefficients for proton movement increase through 395 K. At higher temperatures not all protons are available for fast diffusion and so as the flux of protons decreases even though they are moving more rapidly and the proton conductivity

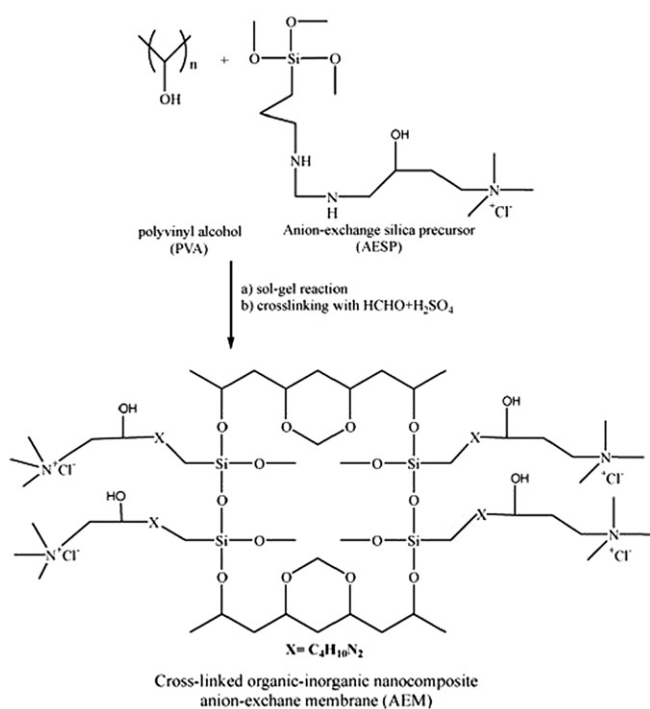


Fig. 16. Schematic route for the preparation of organic-inorganic nanocomposite AEM [81].

of the solid falls. As the temperature is increased a number of distinct hydration phases are observed until a limiting hydration state is reached involving a few very strongly bound water molecules which may be stable up to temperatures > 475 K. It is this limiting hydration state that is of particular interest in the development of intermediate temperature PEM fuel cells as proton conduction in these materials may still involve H_2O but since these H_2O molecules are tightly bound, the system would not need any external humidification. More over HPAs are in general readily soluble in water. As such, use of these materials in fuel cells implies the impossible requirements of retaining hydration to ensure conductivity and removing-product water to prevent dissolution, however, it should be emphasized again that the proton conductivity is not linked to the polymer backbone and hence it is always possible that the stability and durability have to be ensured by proper protection within the polymer matrices but still maintaining the conductivity chain. The fabrication of membranes in this model can be difficult and hence repeatability of the membrane can become one of the issues.

Above 473 K, the HPAs begin to become unstable resulting in an irreversible oxide phase that does not conduct protons. The issue with implementing the HPAs as intermediate temperature proton conductors is that as the temperature increases through ca. 403 K the rate of diffusion increases but the number of protons available for proton conduction decreases resulting in lower values of conductivity. Clearly the HPAs must be dispersed in a composite membrane in such a way that all the protons are available for proton conductivity so that the higher diffusion coefficients available at higher temperatures can be exploited. It should be pointed out that the HPAs are redox active and can be reduced to a series of compounds with unchanged structures, and intense blue colors termed the heteropoly blues that are electronically conductive, but this reduction can be sluggish in the absence of a catalyst. The fuel cell membrane in a working fuel cell is in an oxidative environment, due to the presence of peroxide, the HPAs do not reduce to heteropoly blues in fuel cell membranes except in extreme circumstances. HPAs are in general water soluble, but can be immobilized, by embedding in a silicate matrix, or by covalently linking to an organic moiety in a coordination site in a lacunary HPA. Many metal atoms may be replaced with the lacunary HPA under acidic conditions to reform the HPA skeleton with the metal atom taking the place of W or Mo Oxygen octahedra. When the central atom is silicon or another easily organically functionalized moiety, then this situation provides a facile method of tethering the HPA to a polymer. This approach has been employed in PEMs to provide robust membranes where the HPA is not necessarily immobilized by burying in the silicate matrix [91].

To enhance the mechanical properties and to effectively immobilize the heteropolyacid in the polymer matrix, chemically cross linked nanocomposites of PVA and phosphotungstic acid (PWA) have been prepared by in situ cross linking of the polymer matrix in solution form. The variation of conductivity of these membranes with temperature follows Arrhenius type [92]. PVA membranes doped with PWA have been made [93]. PVA membranes doped with PWA are swelling too strongly to be used. SiO_2 has been added into the PVA/PWA membrane to improve its reagent endurance and thermal stability [94]. The conductivity of salts of silicotungstic acid was studied [95]. The high protonic conductivity is due to mobile proton that is present as an admixture in the crystalline structure of synthesized salt [96] or due to the presence of crystalline water. The nature of the cation has a great influence on the final properties of the salts of Keggin heteropolyacid. The salts containing small cations, such as Na^+ , are soluble in water or in other polar solvents whereas the salts with large cations, such as Cs^+ , are insoluble in water [97]. Their low solubility

is attributed to the low solvation energy of the large cations. Cross linked composite membranes consisting of poly (vinyl alcohol) (PVA) and silicotungstic acid (STA) for use as proton-conducting polymer electrolyte have been prepared by solution casting method. Membrane swelling decreases with increase in cross linking density accompanied by improvement in mechanical properties [98]. Chemically cross linked composite membranes consisting of a poly (vinyl alcohol-co-vinyl acetate-co-itaconic acid) (PVACO) and phosphomolybdic acid (PMA) have been reported. The proton conductivity of the composite membranes is of the order of $10^{-3} \text{ S cm}^{-1}$ which is an order lower than the commercially available membranes. The methanol permeability is of the order of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and is always lower compared to the Nafion membrane measured under similar conditions [99]. Stabilized forms of heteropolyacids (HPAs), namely phosphomolybdic acid (PMA), phosphotungstic acid (PTA), and silicotungstic acid (STA), are incorporated into polyvinyl alcohol (PVA) cross linked with sulfosuccinic acid (SSA). The incorporation of inorganic fillers in PVA–SSA viz., STA and PTA, retard the methanol-release kinetics under osmotic-drag compared to Nafion, although PVA–SSA itself exhibits still lower methanol permeability. The rate of methanol crossover in PVA–SSA–HPA-bridged-mixed-matrix membranes decreases dramatically with increasing current density thus imparting higher DMFC performance in relation to a DMFC using a pristine PVA–SSA membrane. A peak power density of 150 mW cm^{-2} at a load current density of 500 mA cm^{-2} is achieved for the DMFC using a PVA–SSA–STA-bridged-mixed-matrix-membrane electrolyte [100].

1.3.1.5. PVA/zirconium phosphate. Zirconium hydrogen phosphate ($\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$) (ZrP) is a desirable additive. In practice the zirconium phosphate phase may vary from amorphous to crystalline and the proton conductivity of zirconium phosphate can vary from 10^{-7} to $10^{-3} \text{ S cm}^{-1}$ depending on the phase composition, structure, and hydration state.

Water insoluble zirconium phosphate has been added to suppress crack formation due to the shrinkage caused during drying. It also contributes to protonic conduction through the proton of phosphate moiety and crystalline water thereby reducing the humidity dependence on conductivity. Polyvinyl alcohol (PVA) and zirconium phosphate based composite membrane with cesium salts of silicotungstic acid as the active component was described [101]. Water uptake and swelling of the fabricated membranes decrease with increase in cesium content. At 50% of relative humidity, the protonic conductivity of the hybrid membranes is in the range of 10^{-3} to $10^{-2} \text{ S cm}^{-1}$. Two series of composites, i.e., PVA/oxidized starch (OST)/exfoliated a-zirconium phosphate (POST-ZrPn) and PVA/starch (ST)/exfoliated a-zirconium phosphate (PST-ZrPn), have been fabricated using a casting and solvent evaporation method. Compared with PSTZrPn, POST-ZrPn films with the same component ratio have showed higher tensile strength (rb), lower elongation at break (eb) and improved water resistance. Additionally, in the POST-ZrPn series, rb and eb increase with an increase in a-zirconium phosphate (a-ZrP) loading; however, higher a-ZrP loads resulted in the aggregation of a-ZrP particles. Compared with POST-ZrP0, the values for rb, eb, and water resistance of POST-ZrP3, containing 1.5 wt % a-ZrP, are increased by 128.8%, 51.4%, and 30.2%, respectively [102].

1.3.2. Nano particle composite membrane

1.3.2.1. PVA/MMT. The use of Montmorillonite (MMT) in DMFC applications has become quite popular as the exfoliated layered clay particles act as a reasonable barrier for methanol permeation. MMT is a natural, fine ground ceramic material, composed mainly of silica, alumina and water. The chemical formula of MMT is $\text{M}^{n+}_x\text{Si}_y\text{Al}_z\text{O}_{10}(\text{OH})_2$.

$n \cdot y\text{H}_2\text{O}[\text{Mg}_{6-0-x}\text{Li}_x(\text{Si}_{8,0})\text{O}_{20}(\text{OH},\text{F})_4]$ [103]. The majority of work on nanocomposites focuses on MMT because of their swelling properties, high cation-exchange capacities, high aspect ratio and large surface area [104]. Natural montmorillonite is hydrophilic and most polymers tend to be hydrophobic, so the clay surface must be modified to yield organophilic clay in these cases. A low volume fraction of clay improves the mechanical and barrier properties of the pristine polymer, thus making these nanocomposites very promising materials [105]. In order to improve the compatibility of montmorillonite with the polymer and to increase the interlayer spacing, the cations in MMT were exchanged with alkylammonium salts [106]. Just like silica, clays can be functionalized with $-\text{SO}_3\text{H}$ groups via reaction with a functionalized silane, these functionalized materials can be added to the ionomer to produce a membrane with improved proton conductivity and favorable MeOH permeability.

A composite polymer electrolyte membrane composed of a PVA polymer host and montmorillonite (MMT) ceramic filler (2–20 wt.%), was prepared by a solution casting method. The permeability values of all PVA/MMT composite membranes were found to be lower than those of the Nafion 117 membrane. The ionic conductivity values of the PVA/MMT composite polymer membranes are in the order of $10^{-2} \text{ S cm}^{-1}$ at room temperature [107,108]. The incorporation of the sodium montmorillonite nanoclay into sulfonated PVA strongly affects the properties of the nanocomposite membranes. The water uptake, proton conductivity, and methanol permeability of the membranes initially decrease with increase of the nanoclay loading and then increase again upon further addition of the nanoclay. These results might be related to the interaction between sodium montmorillonite and PVA, exfoliation of the nanoclay in the polymer composite, and changes in the degree of crystallinity of the polymer with the nanoclay content. The optimum level of layered silicate sodium montmorillonite is achieved at which the maximum C/P ratio of the nanocomposite membrane was 2% (w/w) [109].

1.3.2.2. PVA/CNT. All the reports are primarily intended to use CNTs as mechanical stability booster or reinforcing phases albeit in small amounts. However, CNTs can be functionalized on the sidewalls with desired groups through careful chemical process, which can be used in a constructive manner to increase the conductivity of membranes.

Polyvinyl alcohol, sulfonic acid functionalized CNT and fluorinated MMT containing composite polymer electrolyte membrane have been reported [110]. The strategy of using both sulfonated CNT and fluorinated MMT is to increase sulfonic acid content with highly hydrophobic fluorinated surface of the membrane. The result shows that water uptake can be controlled by using hydrophobic–hydrophilic interaction to reach a balance.

1.3.3. Hybrid organic inorganic composite membrane

The hybrid composite membrane material by bridging organic and inorganic chemistry at a molecular level is linked to synergetic effects of organic and inorganic matrix with desired and improved properties in comparison to own unique properties of each components. A simple way of synthesizing these types of membrane is the physical blending of two components in an appropriate solvent. During the synthesis process care should be taken to avoid the unwanted precipitation of the components.

The high performance poly (vinyl alcohol)/titanium oxide nanotubes/poly (styrene sulfonic acid) (PVA/ntTiO₂/PSSA) proton-conducting composite membrane was prepared by a solution casting method [111]. The ionic conductivities of the blend composite membranes are of the order of $10^{-3} \text{ S cm}^{-1}$ in water at ambient temperature. It is found that the methanol permeability of

the PVA/ntTiO₂/PSSA composite membranes (on the order of $10^{-7} \text{ cm}^2 \text{ s}^{-1}$) is lower than that of Nafion 117 membrane (on the order of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [111]. PVA/PSSA/MA/Clay hybrid membranes containing sulfonic acid and carboxylic acid groups were synthesized [112]. Sulfonic acid groups are introduced into the PVA matrix by esterification with poly (styrene sulfonic acid-co-maleic acid) (PSSA-MA). In addition, the modified clay such as Clay Na⁺, Clay 30B, and Clay 15A particles are dispersed into the polymer matrix. The membrane with Clay Na⁺ has low amount (by vol.%) of clay than others due to high specific gravity. Therefore, the membrane with Clay Na⁺ (2.86 g cm⁻³) showed the highest methanol permeability while the membrane with Clay 15A (1.66 g cm⁻³) showed the lowest methanol permeability. The water swelling and proton conductivity of the hybrid membrane with Clay 30B are affected by organic modifier of Clay 30B. The membrane with Clay 30B has shown the highest water swelling and proton conductivity [112]. Novel modified chitosan (NCBC)-silica-PVA nanocomposite membranes with varied NCBC-silica content and cross linking density have been prepared, in which highly acidic $-\text{SO}_3\text{H}$ groups are grafted on the inorganic segment (less swellable) while less acidic $-\text{COOH}$ groups are grafted on the organic segment (high swellable) for achieving highly proton conductive and stable polyelectrolyte membranes [113]. Physicochemical and electrochemical properties of these membranes depend on the NCBC-silica content in the membrane matrix as well as the cross linking density. Developed membranes show good stabilities, flexibility, and water retention capacities. It is observed that the methanol permeability and conductivity at elevated temperatures were governed by the concentration of bound water. Observed proton conductivities ($1.92\text{--}5.31 \times 10^{-2} \text{ S cm}^{-1}$) of NCBC-silica-PVA cross linked membrane at ambient temperature dramatically increase at high temperatures, in comparison to Nafion 117 membrane, due to the activated thermal conduction process. This advantage can be exploited in high temperature applications. A method for the preparation of organic/inorganic hybrid membranes based on PVA and sulfonated POSS (sPOSS) has been reported [114]. This simple method involves solution blending of PVA and sPOSS, followed by cross linking with EDTAD. The proton conductivity increases while methanol permeability decreases with increase in sPOSS content in the hybrid membranes. More specifically, the proton conductivity of the PVA/sPOSS hybrid membranes increases with sPOSS content, reaching 0.042 S cm^{-1} when the sPOSS content is 50 wt% in the hybrid, more than double that of Nafion 117. Furthermore, the methanol permeability of the membranes decreases with increasing sPOSS content, reaching a value about one order of magnitude lower than Nafion 117 for the hybrid containing sPOSS 50 wt%. Organic–inorganic hybrids, based on PVA/SiO₂ hybrid membranes containing sulfonic acid groups, were prepared using the sol–gel process under acidic conditions. The PVA/SSA/silica hybrids and PVA/SSA membranes that do not contain any silica were investigated on their proton conductivity and methanol permeability. Both these properties are dependent on the SSA content both as a cross linking agent and as a donor of hydrophilic SO_3H groups. Both the proton conductivity and the methanol permeability decrease with SSA concentration up to about 20 wt%, and above this concentration, these properties increase with SSA content. The hybrid membranes are more effective as methanol barrier. In particular, the free water is reduced by the presence of silica particles in the organic polymer matrix, compared to the membranes that do not contain any silica. Therefore, it is suggested that the methanol permeability can be reduced by controlling the free water content in the membrane. The methanol permeabilities through the PVA/SSA/silica membranes are proportional to the proton conductivities. The proton conductivities of the PVA/SSA/silica membranes are in the range of $10^{-3}\text{--}10^{-2} \text{ S cm}^{-1}$, and the

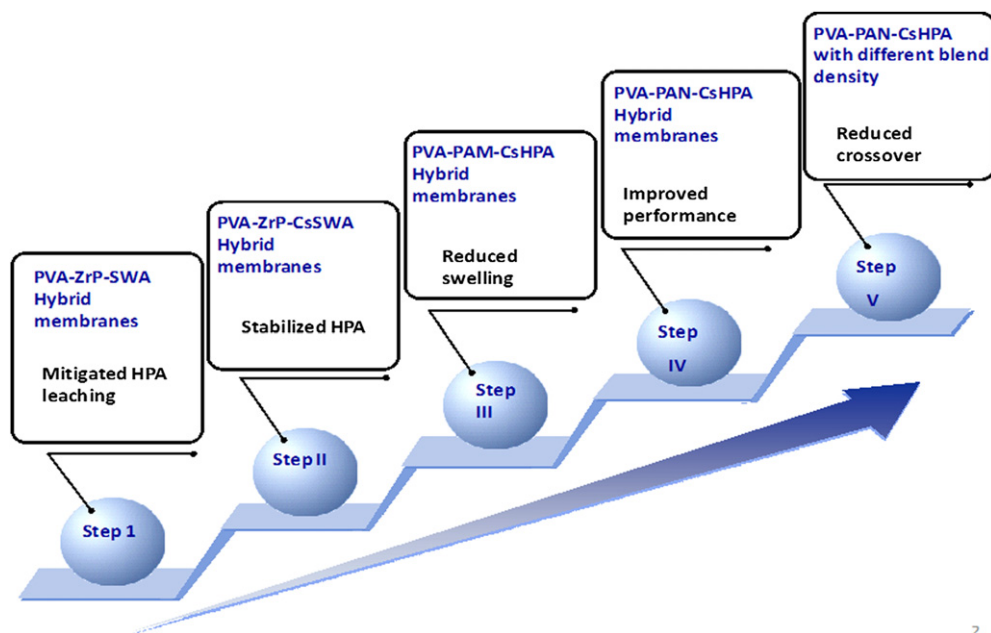


Fig. 17. Step wise design of a membrane for DMFC application [adopted from ref. [2].

methanol permeabilities range between 10^{-8} and 10^{-7} $\text{cm}^2 \text{s}^{-1}$. The hybrid membranes may be suitable for DMFC applications [115]. Cross linked poly(vinyl alcohol) (PVA)/poly(acrylic acid) (PAA)/silica hybrid membranes have been prepared to evaluate the possibility of use as a proton-exchange membrane for direct methanol fuel cell (DMFC). Noticeably, the methanol permeabilities are reduced by cross linking between PVA, PAA and SSA chains without a large sacrifice of proton conductivity [116]. The composite membranes based on polyvinyl alcohol (PVA), sulfonated poly ether ether ketone (SPEEK) and phosphotungstic acid (PWA), have been reported [117]. The composite membranes have shown proton conductivity in the order of 10^{-3} S cm^{-1} . The proton-conducting membranes with novel microstructure based on partially phosphorylated poly(vinyl alcohol) (P-PVA) and polyethylene glycol (PEG) grafted silica (PEG-SiO₂) particles have been reported to retain the proton conductivity and work under high temperature or low-humidity conditions. The PEG-SiO₂ particles have been synthesized through acid catalyzed hydrolysis and condensation reactions. In these membranes, P-PVA acts as the proton source and PEG acts as the proton solvent. The PEG rich phases in the hybrid membrane form continuous ionic conducting pathways and subsequently give high ionic conductivity [118]. Sulfonated mesoporous benzene-silicas are introduced into a PVA matrix [119]. Highly ordered 2D hexagonal mesoporous benzene-silicas were prepared using 1,4-bis(triethoxysilyl)benzene (BTEB) organosilica precursor and two kinds of organic templates, such as an octadecyltrimethylammonium bromide (ODTMA) and a Pluronic P123 poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer. The benzene-bridged silsesquioxane has both hydrophobic and hydrophilic properties, and the additive sulfonic acids can be attached to the benzene-bridging groups by the post treatment step. The benzene moieties increase the thermal and mechanical stability, which are the weak points of the PVA matrix. Above all, mesoporous materials have the advantage of retaining water even at a high temperature, due to the capillary force of the mesopores, and the large number of pores arranged in hexagonal patterns can be used as tunnels to transport protons. The ODTMA-driven mesoporous benzene-silica has a pore diameter of 2–3 nm and shows mixed morphologies composed of

agglomerates of spherical particles with a particle size below 100 nm and thin rods with a thickness on the nanometer scale. On the other hand, the P123-driven material has mesopores with a pore diameter of 6–7 nm and shows cylindrical rod-type morphology and its bundles; however, their thickness and length scales are not uniform in the range of 1–100 μm . PVA and mesoporous benzene-silica are mixed with each other by using a cross linking agent sulfosuccinic acid (SSA). The physical and chemical characterization of the hybrid electrolyte membranes are performed by varying the contents of sulfonated mesoporous benzene-silicas and SSA. All the hybrid membranes studied have shown good performance in lowering the methanol crossover (i.e., ~68% reduction in comparison with the Nafion 117 membrane), and mesoporous benzene-silica with smaller particle morphology and pores (2–3 nm) is observed to be a more effective additive. The morphology and pore size of the mesoporous benzene-silica materials are crucial factors to control the transport behavior with respect to methanol and the protons [119].

2. Stability, durability and long term performance of PVA based membranes

PVA based membranes have been shown to be stable up to 400 °C in some cases [129]. They have been shown to be durable over extended periods of operation in fuel cells and the available data show that these membranes are durable for periods over 70 h and up to one week [45]. The cells incorporating these membranes have delivered power in the range of 15–45 mW cm^{-2} in the temperature range of 30–80 °C showing that these membranes are good enough for the power requirements.

3. Economic and ecological aspects of PVA based membrane

Even though a direct harmonized economic evaluation of the available membranes for fuel cell applications will be useful, such a direct comparison of the economics is not immediately available due to various reasons. In the case of membranes a variety of factors contribute to the economics of the membrane. In general, in

Table 4

Comparison of the PVA based membranes for the critical membrane properties.

Membrane materials	RH %	Temperature (°C)	Conductivity (S cm ⁻¹)	Permeability (cm ² s ⁻¹)	Ref
PVA-PAN-CsSWA-Glu	50	RT	5.3×10^{-3}	7.8×10^{-8}	[2]
PVA-PAN-CsPWA-Glu	50	RT	6.8×10^{-3}	1.8×10^{-7}	[2]
PVA-PAN-CsPMA-Glu	50	RT	93×10^{-3}	2.3×10^{-7}	[2]
PVA-ZrP-SWA	60	60	10^{-2}	6×10^{-7}	[2]
PVA-ZrP-Cs ₁ SWA	50	100	0.013	2×10^{-6}	[2]
PVA-ZrP-Cs ₂ SWA	50	100	0.02	3×10^{-6}	[2]
PVA/PWA/SiO ₂	—	—	0.004–0.017	10^{-7} to 10^{-8}	[94]
Si/SPS/A-20PVA/20PWA	—	25	0.038	6.38×10^{-8}	[120]
PVA/MMT/PSSA	—	25	$2-7 \times 10^{-3}$	$\sim 10^{-7}$	[121,122]
CPVS 3	—	—	—	8.5×10^{-7}	[123]
SPVA18.2-0m	—	25	0.7×10^{-2}	4.6×10^{-7}	[124]
PGA-H ₃ PO ₄ -0.7PVA	100	120	6×10^{-3}	—	[125]
PVA/PWA/PTMO/H ₃ PO ₄ (10/1/70/5 wt%)	75	0	4.8×10^{-3}	—	[128]
PVA/SiWA/MPTS/H ₃ PO ₄ (50/10/10/30 wt%)	75	80	8.5×10^{-3}	—	[126]
PVA/GLA/SBA-Ph-SO ₃ H	—	170	0.0077	—	[127]
CL-SEC/PVA	—	25	0.017	—	[128]
PVACO/PMA	—	30–100	10^{-3}	10^{-6}	[97]
Nafion [®] 115	100	90	0.03	3.5×10^{-6}	[2]

conventional separation process, PVA based hybrid membranes are economically advantages.

The cost estimates on the membranes are not that easy. In general, it can be said that from the point of view of operating cost and energy requirements, hybrid membranes may score over other membranes but from the point of view of investment costs, the economics depends on the type of materials included in hybrid membranes. The same can also be stated with respect to the fabrication of the hybrid membranes. Hybrid membranes may not be economical for small scale operations due to complexity, but overall, integration of hybrid process may prove to be advantageous for long-term use [130].

From the ecological aspect, PVA membrane does not release any toxic gases or cause any hazard to environment. It does not require any organic solvent for preparation of membrane. By simply dissolving the polymer in water, membrane can be achieved. So there is no harmful effect to the health of the workers.

4. General analysis of PVA based membranes with respect to Nafion[®]

- PVA based membranes and other composite membranes give the flexibility on the inclusion of proton-conducting materials and hence are amenable for control of thermal and mechanical behavior of the membrane [55].
- The size and shape control of the proton-conducting material is possible in these membranes while in Nafion, the proton is stitched to the film forming polymer architecture [112,119].

- Though the multi-component systems can exhibit cumulative behavior with respect to the properties, they are susceptible to dissolution, leaching, or other degradation processes [64].
- Conceptual possibilities have to be evolved in the case of these membranes since proton conducting species are separate from the polymer and increasing conductivity of the membrane is not as competitive as that of Nafion. The proton in Nafion is in a highly electronegative environment and hence its conductivity is tremendously higher than any other membranes [3].
- Other membranes have to synergize the hydrophobicity (provides the mechanical stability) and hydrophilicity (responsible for facile proton conductivity), while in the case of nafion this is inherent in the two domains of its backbone [131].
- In the case of Nafion the conductivity is mainly by Grotthus hopping mechanism while in other membranes both Grotthus and vehicular transport and hence conductivity values may not reach that of Nafion [129].
- Membranes other than Nafion are better from the point of view of hydration stability at high temperatures, low fuel crossover, mechanical, thermal and oxidative stability [69–72].
- More precise knowledge has to evolve on the structure, degree of crystallinity, shape and dimension of the particles, and their distribution in the polymer matrix for possible predictive exploitation of these membranes for fuel cell applications [77].
- Though, tremendous effort has been invested in polymer based membrane development, more efforts are required to obtain a clear understanding of the mechanisms that are responsible for the observed transport properties in these membranes [129].

Table 5

Characteristics of commercial and composite membranes for DMFC applications.

Membrane	Water uptake (%)	IEC (meq g ⁻¹)	Methanol diffusion coefficient (cm ² s ⁻¹ × 10 ⁻⁶)	DMFC performance	Proton conductivity (S cm ⁻¹)	Ref
Nafion 117	21	0.9	1.7	OCV = 0.65 V 100 mA cm ⁻² (0.5 V, 70 °C 2 bar air 2 M)	0.095 (25 °C)	[132–134]
CRA-08	33.7	1.4–2.2	0.6	—	0.045b(60 °C)	[135–136]
Ion Clad R1010	—	1.2	0.6	—	0.146 (60 °C)	[134,137]
SPEEK	30	1.7	1.75	25 mA cm ⁻² (0.5 V 80 °C, 2 M)	0.013 (60 °C)	[138–140]
Composite membrane	40–80	2–3	0.01	OCV = 0.75 V 160 mA cm ⁻² (0.35 V)	0.1–0.93 (90 °C)	[87,91,94,101, 132,141,142]
PVA or PVA based membrane	50–90	0.5–0.8	0.08–4	Low methanol permeability 6.8 mW cm ⁻²	0.01 (80 °C)	[56,110]

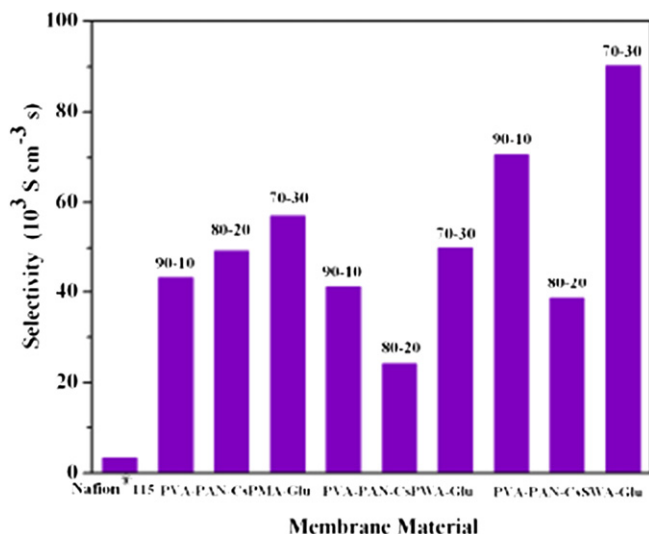


Fig. 18. Selectivity for various PVA based membranes with that of Nafion-115 [2].

- The fillers normally employed in the polymer based membranes may also show reduced methanol crossover due to catalytic decomposition of methanol and this aspect has to be firmly established [3].

5. Challenges and perspectives

The critical requirement for the successful development of new membrane materials are detailed in the following. High ionic conductivity is the essential requirement and main deciding factor for membranes for DMFC application. In designing new types of PVA based polymers one should keep in mind how one can lower down the water content by retaining good ionic conductivities. In the development processes, inorganic material should be accommodated in the organic matrix in such a way that it should permit the utilization of maximum elementary functions in a small volume, and hence optimize complementary possibilities and properties of the inorganic and organic components.

It is believed that the development of PEMs via water-soluble polymer blend may provide more environment-friendly and cost-effective process for membrane preparation since the use of harmful organic solvent can be minimized and also the process is relatively simple. However, the enhancement of long-term and thermal stabilities of this type of PEM may be needed for its more successful applications. Recently hybrid and copolymer type architecture are placed on strategies to control the molecular structure of polymers that bear ionic and hydrophobic segments and on the influences of phase separation on selected properties pertinent to fuel cell performance. More recently, combining ionic liquids with block polymers has been made as a unique platform for designing new polymer electrolyte membrane with improved properties. This class of materials is only opening a new direction of research to be explored. More detailed analyses for the relation between microstructure and the transport properties under real fuel cell condition are in progress. Especially, systematic investigations to establish the relationship between the temperature-dependent swelling and the corresponding transport properties (solvent permeation/electro osmotic-drag, etc.) have been carried out for DMFC applications.

Direct methanol fuel cells (DMFCs) are attractive power sources for portable and stationary applications. One of the challenges for

commercializing DMFC technology is to develop less expensive, non-fluorine based membrane material, with no or limited cross-over of methanol through the membrane (a process that decreases the performance of cathode and leads to fuel loss). In order to alleviate the problems associated with the state of the art Du pont product Nafion[®], such as environmentally unfriendly fluorine based production, methanol crossover and low dimensional stability at high temperatures and low humidified operations of a fuel cell, spurt of research activities are focused to develop an alternate membrane possessing appreciable proton conductivity, low swelling and low diffusion for methanol by a simple and environmentally benign fabrication method.

As Nafion[®] holds the utmost electronegative environment possible in a chemical system, it is nearly impossible to design a membrane that will have better ionic conductivity compared to Nafion[®]. Realizing this limitation, it was considered worthwhile to design a membrane which may possess ionic conductivity less than that of Nafion[®], but should have at least one property (for fuel cell applications) better than that of Nafion[®]. Since the fuel crossover from anode to the cathode drastically reduces the performance in a DMFC, it was considered that the membrane development must mainly focus on this aspect of fuel crossover. In this direction, hybrid membranes with PVA as polymer constituting matrix and with variety of additives either another polymer or inorganic substances have been developed and these are reviewed in this presentation.

A simple stepwise strategy for formulating PVA based membranes with appropriate characteristics for DMFC application using heteropoly compounds as proton conductors is illustrated in Fig. 17 [2]. It is seen that systematic rationalization, designing and appropriate fabrication methodologies have been adopted to achieve the desired properties in terms of conductivity, swelling, methanol permeability and also required thermal and mechanical stability. In Table 4 the summary of the essential characteristics of PVA based membranes are compared with that of Nafion-115. It can be seen that all the desired characteristics can be nearly realized in PVA bases membranes for DMFC application. The comparative merits of various commercial composite membranes for DMFC applications are summarized in Table 5. It is demonstrated in Fig. 18 that the PVA based membranes have attained necessary levels of maturity for DMFC applications in terms of the methanol crossover function. Therefore, the possibility of realizing DMFC as an energy conversion device in the near future appears to be bright.

6. Conclusions

The foregoing presentation shows that the chemistry of PVA based membrane is one of the subjects of intense research and is almost reaching certain maturity levels so as to be adopted in practical devices. For the two essential characteristics for membrane application namely proton conductivity and methanol crossover, PVA membranes are becoming competitive with respect to the state of art Nafion membranes. There may be a need to develop theory between molecular structure, morphology and membrane properties. The credo of creativity on PVA based polymer electrolyte membranes may soon lead fuel cell from laboratory to the real world application.

Acknowledgments

This work was supported by Priority (NRF) funded by the Ministry of Research Centers program through the National Research Foundation of Korea Education, Science and Technology (2009-0093823). This research was financially supported by a grant of MEMS Research Center for National Defense funded by Defense

Acquisition Program Administration. We are also grateful to Defense Nano Technology (Center) for supporting this research work.

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